THE CATALYZED ISOMERIZATION AND DIMERIZATION OF UNSATURATED FLUOROCARBONS

By

FRED NORMAN TLUMAC

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

June, 1961

ACKNOWLEDGMENTS

The NMR spectra were prepared and interpreted by Dr. W. Brey and his associates at the University of Florida.

The C_5F_8 isomers and the C_6F_{12} isomers were separated by vapor phase chromatography. The equipment and technique were provided by Dr. T. M. Reed III and his group at the University of Florida.

Dr. R. D. Dresdner provided the opportunity to pursue a graduate study and the guidance to complete it. The author is therefore deeply indebted to Dr. Dresdner.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
INTRODUCTION	1
EXPERIMENTAL	8
Analytical Equipment Utilized	8
General Reaction Procedure	12
Synthesis of N_2F_4	13
Reactions of $CF_2=NCF_3$	17
Reactions of C_3F_6 over Cesium Fluoride	23
Reaction of $CF_2=CFCF_2CF=CF_2$ and NF_3	28
Reactions of C_5F_8 Isomers over Alkali Metal Fluorides	30
DISCUSSION	52
The Synthesis of N_2F_4	52
Effect of Alkali Metal Fluorides on C_3F_6	57
Effect of Alkali Metal Fluorides on $CF_3CF_2CF_3$, $CF_3CF=CFCF_3$ and CF_3CN	65
Effect of Cesium Fluoride on $CF_2ClCFClCF_2CF=CF_2$	66
Effect of Alkali Metal Fluorides on $CF_2=NCF_3$	67
Effect of Alkali Metal Fluorides on the Isomerization of $CF_2=CFCF_2CF=CF_2$	71
CONCLUSIONS	84
BIBLIOGRAPHY	87
BIOGRAPHICAL SKETCH	90

LIST OF TABLES

TABLE		Page
I.	Infrared Absorption Spectra	50
II.	Nuclear Magnetic Resonance (NMR) Spectra	51
III.	Isomerization of C_5F_8 Isomers over Selected Catalysts	76

INTRODUCTION

In 1941, J. H. Simons provided a group at Columbia University with a sample of fluorocarbon.[1] Utilizing the properties of this small sample, the necessary liquid and solid fluorocarbons were developed for the Manhattan Project.[2] The thermal stability and resistance to chemical reactions[3] make fluorocarbons highly desirable as greases, oils, aerosol carriers and building materials. The lack of chemical reactivity, however, has forced the fluorine chemist to devise new routes of syntheses.

The hot tube reaction is a method commonly employed by fluorine chemists. Usually the material is passed through a tube packed with an inert material. The tube is heated to a temperature that causes at least one of the materials to cleave. Products are obtained that are the result of cleavages, and sometimes recombination. The "hot tube chemist" has available only a certain number of variables by which he can alter the reaction. He can vary the reactants, the temperature, the pressure, the contact time and medium in which the reaction is to be initiated.

The combinations of reactants that are available are unlimited. Pressure usually exerts an influence on the distribution of products, as does temperature and contact time. The real difficulty is that the temperature required to activate a fluorocarbon generally results in carbon-carbon bond cleavage.

It is evident that a method of reducing the activation energy of fluorocarbon systems is needed. This has probably been done for years by chemists who placed "inert" materials in their reaction tubes. There have been, of course, many successful hot tube reactions, but many more would have been successful if a catalyst, or a better catalyst had been employed. Sodium fluoride is a common packing material for reactor tubes. There has been some question as to whether or not this packing is inert. Actually, sodium fluoride is the least-active catalyst of a group that are effective catalysts - the alkali metal fluorides.

Gens[4] observed the isotopic exchange between solid inorganic fluorides and gaseous fluorocarbons. Carbon tetrafluoride did not undergo this exchange, but perfluoropropylene was an active exchange agent.

The alkali metal fluorides were found to undergo exchange most readily. As the atomic number of the cation was increased, the temperature at which rapid exchange was observed was decreased.

A rapid and a slower exchange were observed and Gens postulated that two distinct mechanisms were involved.

The rapid exchange was much too rapid to involve just fluorine atoms or ions on the surface of the crystals, and he concluded that there was rapid migration of fluorine atoms to defect sites on the surface of the crystal.

When the exchange tube was heated to roughly one-half the absolute melting point of the metal fluoride, the slower exchange was observed. Whereas the rapid exchange exhibited an exponential increase in exchange rate with temperature, the slower exchange mechanism caused the exchange rate to increase at constant temperature. Gens proposed that the rate-controlling step in this mechanism was an ionic self-diffusion of fluoride ions through the crystals to the surface.

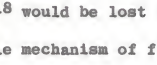
Miller[5,6] has observed ionic reactions between halocarbon olefins and alkali metal fluorides. He demonstrated that by a prudent choice of solvents, the fluorine ion could replace the chlorine in an olefin, or conversely, a

chlorine ion could replace fluorine. Miller gave very good evidence for a S_N2' mechanism. This involved a negative ion addition to a double bond and a shift of electrons, forcing off a negative ion from the allylic position. This mechanism is generally considered to be concerted. Miller's work indicated that perfluoropropylene exhibited the same type of mechanism, but substitution of one material other than fluorine on perfluoropropylene yielded only one product, $CF_2XCF{=}CF_2$. So the mechanism could not be definitely established.

If the slower exchange mechanism proposed by Gens did involve an attack on perfluoropropylene by a fluoride ion of the CsF crystals, it is energetically essential that a fluoride ion be returned almost spontaneously to the crystal system. Gens observed that the contribution of the slower or ionic exchange to the total exchange was very small. The technique involved, however, made no provision for re-exchange, as it measured only total exchange. If an S_N2' attack was the mechanism on the isotopic exchange, the choice of perfluoropropylene would have resulted in a much lower observed exchange.

In the initial attack, the unstable intermediate had one chance in six of returning the F^{18} ion to the CsF crystal system. If the same molecule was again attacked by an F^{18} ion, there would be the same one chance in six that the attack would not be successful, and if it were, there would be one chance in three that the original F^{18} (now in the allylic position) would be lost. As the substitution of F^{18} for F^{19} increased, the probability increased that an F^{18} would be lost instead of an F^{19} ion.

Another possible mechanism of fluoride ion attack is the formation of a carbanion.



Again, many possibilities exist for re-exchange, and the observed rate may have been lower than the actual exchange rate. Any stability the carbanion might have could be attributed to its association with the CsF crystals. The fluorine from the center carbon would migrate as an ion into a hole or defect in the crystal lattice.

The feasibility of the ionic exchange between alkali metal fluorides and fluorocarbons is strengthened by Gens' observation that perfluoropropylene exchanged, and carbontetrafluoride did not. Carbontetrafluoride is not known to undergo ionic reactions;[7] whereas perfluoropropylene as mentioned above probably does undergo S_N2' substitutions in solvents. The transfer of the reaction medium from a solvent solution to a heterogeneous condensed phase on a solid would add one further requirement. Some form of association between the unstable intermediates proposed and the alkali metal fluoride crystals must exist,[8] or the exchange observed by Gens will not result in catalysis, but merely in the exchange of fluorine atoms and ions.

Christie[9] first observed the catalytic effect of alkali metal fluorides on the oxidation of perfluoropropylene. Dresdner[10] studied the catalyzed reaction of nitrogen trifluoride and perfluoropropylene.

The purpose of this research was to study all known examples of alkali metal fluoride catalysis, evaluate the results and then perform experiments designed to answer the following questions:

1. What types of reactions are catalyzed by alkali metal fluorides?

2. What conditions are required for catalysis?

3. Can a satisfactory mechanism be proposed that explains both the conditions required and the materials produced?

EXPERIMENTAL

Analytical Equipment Utilized

Distillation column (-60° to +16°)

This column consisted of three separate pieces, each piece being fitted with standard tapered joints. The head was a dewar-type container which could be cooled with a Dry Ice-acetone mixture. The column tube length was 55 cm., and inside diameter was 0.8 cm. The tube had a silvered vacuum-jacket, and was packed with 0.16 cm. inside diameter, single turn, stainless steel helices. The design included a vapor take-off. All temperatures in this paper were recorded in centigrade units. The column had 30 theoretical plates, but would have a somewhat lower value for fluorocarbons.[11]

Distillation column (+28° to +100°)

This column consisted of three separate pieces connected by standard-taper ground glass joints. Temperature was read with a thermometer. Heating was accomplished by a mantle under the pot, and by a helical heating wire on

the column. The column featured a liquid take-off, and a head which could be cooled by Dry Ice-acetone or circulating ice water. The tube was packed with 0.16 cm. single turn, stainless steel helices. The column had 15 theoretical plates, slightly less for fluorocarbons.[11]

Infrared absorption spectra

Two instruments were used for infrared absorption data. All samples were in the gas phase unless otherwise noted. A gas cell with NaCl windows, 5.0 cm. long, was employed. All recordings were made at 25° and pressures of 4 mm. to 20 mm. The instruments employed were a Perkin-Elmer Model 21 double-beam spectrometer and a Perkin-Elmer Infracord Model 137.

Nuclear magnetic resonance (NMR)

A standard Varian Associates, high resolution spectrometer was employed. The operating frequency was 56.4 mc. and trifluoroacetic acid was used as the external reference. Positive values refer to higher magnetic field. The spectrometer was operated, and spectra interpreted by Dr. W. Brey and his group at the University of Florida.

Vapor phase chromatography

A Perkin-Elmer Vapor Fractometer Model 154-B was used

for all analytical chromatograms. The columns were packed with n-hexadecane, the ethylester of Kel-F acid 8114, or dinonyl phthalate on Celite (65 to 100 mesh). The flow of nitrogen was maintained at 8 cc. per minute. Development times ranged from five to fifteen minutes.

The preparative scale vapor fractometer was constructed by Dr. T. M. Reed III and workers at the University of Florida for quantity separations. An eleven meter column, packed with n-hexadecane was used. The inside diameter of the tubes was 0.63 cm. Nitrogen was used as a carrier. The procedure followed was similar to that reported by Reed.[12]

In order to obtain a representative sample of the gas being analyzed, the entire product, generally 3 to 10 grams was vaporized into a bulb with a volume of 5.4 liters. The pressure in the bulb seldom exceeded 300 mm. and usually was in the range of 50 to 120 mm. Gases were then allowed to mix by diffusion for several hours. Sampling was accomplished by opening the stopcock of the bulb into the evacuated manifold of the vacuum system. The bulb stopcock was then closed and the material in the manifold was condensed into a small ampule attached to the manifold by rubber tubing. The tubing was then clamped and the ampule

removed from the system. The volatilization of all components in the sample was assured by immersing the ampule completely in water at 100°. The pressure in the ampule then exceeded one atmosphere and a gas sample was taken with a syringe and needle by piercing the rubber tubing.

The C_5F_8 isomers were analyzed on a column packed with dinonyl phthalate on Celite. The column was two meters long, and the temperature was maintained at 33°. A flow of 3.6 arbitrary units was maintained on the meter. Nitrogen was used as the carrier gas.

The area under a chromatographic peak is proportional to the product of the amount and the thermal conductivity of the material. The thermal conductivities of the C_5F_8 isomers were checked by feeding known mixtures into the column. The deviations between peak area and mole per cent were less than the precision obtained in integrating the peaks.

The appearance time of each isomer differed enough to make identification of the isomer unquestionable. In very few instances did the peaks fail to resolve. The only exception to this was isomer mixtures containing perfluoromethylcyclobutene-1 and perfluoromethylcyclobutene-3,

which overlapped at all concentrations to some extent. However, perfluoromethylcyclobutene-3 was seldom a reaction product, and was always present in such small quantities that it never interfered with the analyses.

General Reaction Procedure

If the starting material boiled below 0°, it was stored in a cylinder and allowed to escape through a flow meter into the reactor tube. The reactor tube was in all cases nickel and contained either granular carbon, sodium fluoride or cesium fluoride. The reactor tube was heated by an electric furnace, and its temperature was determined by use of an alumel-chromel thermocouple. The temperature was controlled by regulating the voltage to the furnace. The products were collected in a trap, cooled by liquid air, and protected from the atmosphere by a drying tube.

If the starting material boiled above 0°, it was condensed in a bubbler and maintained at 10° below its boiling point by an appropriate bath. Dry helium was bubbled through the liquid at a rate necessary to obtain the mass flow rate of material desired.

Contact times were calculated by dividing V_r (free

volume of the reactor) by V (volume of feed gas per second). The theoretical contact time at one atmosphere may be calculated by the equation:

$$C.T. = \frac{\text{Volume of reactor - Volume of catalyst}}{\frac{\text{moles/hour}}{\text{3600 seconds/hour}}} \cdot 0.082 \cdot T \cdot 1 \text{ atmosphere}$$

$$C.T. = \frac{3600\ V_r}{n/\text{hour} \cdot 0.082 \cdot T}$$

Synthesis of N_2F_4

The NF_3 used in this work was produced in a Simons Electrochemical Cell from pyridine.[13] The impure gas was scrubbed in a closed system with aqueous KOH and KCl and finally H_2SO_4. The NF_3 was then passed through P_2O_5 twice and carefully de-gassed. It was essential that air and other oxygen-containing materials be excluded from this work at all times.

Reclaimed NF_3 from a previous production of N_2F_4 could be used if, in addition to the preparation described above, the gas was scrubbed with a solution of $Fe_2(SO_4)_3$.

The reaction system consisted of a cylinder of NF_3 equipped with a needle valve, a mercury flow meter and a manometer on the inlet side of the reactor. The reactor was a steel tube 61 cm. long (inside diameter 2.54 cm.),

fitted with a nickel head and sealed with a rubber gasket. The head had a nickel inlet and outlet tube, each with an inside diameter of 0.79 cm. The inlet tube acted as a bubbler and extended to 0.6 cm. from the bottom of the reactor. The outlet tube originated at the top of the reactor. The outside of the steel reaction tube was equipped with copper tubing for cooling, which insured the condensation of mercury vapor. An insulated thermocouple was mounted three inches from the bottom of the tube, and the lower half of the tube was wrapped with heating tape. Products were collected in a liquid air-cooled glass trap. Moisture and air were excluded from the reactor by using a tee after the product trap; one side was attached to the product trap, one side to a flow of dry helium and the third open to the atmosphere.

In a sample run, 616 grams of mercury were placed in the tube and the tube heated to 319° while dry helium passed through the entire system. The NF_3 cylinder was then connected and the helium source attached to the outlet tee. The flow of NF_3 was determined from a previously-calibrated flow meter. The temperature of the tube had to be regulated, as it increased during the reaction. Earlier work indicated that temperatures greater than 330°

caused degradation of the product.

At the end of six hours, the NF_3 flow was discontinued and helium was used to flush the system of NF_3 and product. Helium was pumped from the product trap, and the products were transferred to a vacuum system.

Separation of products was accomplished in a vapor take-off, jacketed column in a helium atmosphere. The head was cooled with liquid air. All materials that did not freeze at -185° refluxed off the head. Vapor was taken off slowly until there was no further reflux. The column head was then allowed to warm and the remaining material was transferred into a vacuum system.

Although N_2F_4 is soluble in NF_3, the difference in boiling points probably prevented N_2F_4 (boiling point -73°) from reaching the head until most of the NF_3 (boiling point -128°) had been removed. An infrared absorption spectrum of a sample of mixed products indicated the presence of N_2F_2 as an impurity.[14] As trans N_2F_2 would be unstable at 330°, only the cis or high boiling isomer was present. This isomer boils at -105.7° and melts at less than -195°, so would appear in the low-boiling, low-melting fraction of the separated materials. This fraction was primarily unconverted NF_3.

The higher-melting fraction consisted primarily of N_2F_4, but contained some trace impurities. The trace impurities were removed by condensing the fraction in an ampule containing broken glass. The ampule was immersed in a Dry Ice-acetone bath, and the vapor removed until the vapor pressure of the ampule was 250 mm. The impurities reacted with the glass to give a white product which decomposed on heating, or sufficient lowering of the pressure, to produce a gas and a white solid residue. N_2F_4 was recovered as a fluffy white solid when cooled in liquid air. Upon warming, this solid melted to a colorless liquid.

Oxygen-containing materials had to be prevented from coming into contact with the product at all times. Any laxness caused the formation of colored products. The resulting N_2F_4 after physical separation was at times wine-colored solid that melted to a red-purple liquid. The color was probably $\cdot NF_2$, which has been characterized by Colburn.[15]

In six hours of operation 50 grams of NF_3 flowed into the reactor. The product trap yielded 14 grams of NF_3 and 16 grams of N_2F_4. The conversion was therefore 72.5 per cent. For the reaction:

$2Hg + 2NF_3 \longrightarrow N_2F_4 + Hg_2F_2$

.51 moles $\longrightarrow$ .255 moles calculated

.51 moles $\longrightarrow$ .154 moles actual

Yield = 60.4 per cent

N_2F_4 was identified by molecular weight (103.5, calculated, 104), boiling point range and infrared absorption spectra.[14]

Reactions of $CF_2=NCF_3$

Dimerization of $CF_2=NCF_3$

A reaction tube was packed with CsF and heated to 340°. Azomethine was allowed to pass through the tube at a rate of 1.5 grams (0.011 moles) per hour. The contact time was 200 seconds. The products were collected in a liquid air-cooled trap. After the reaction was completed, the products were transferred to a vacuum system. A simple separation was accomplished by refluxing the material from a condenser that was held at -20°. The lower-boiling material had a molecular weight of 135, and had the proper infrared absorption spectrum for azomethine. This fraction weighed 1.4 grams. The higher-boiling material had successive molecular weights

of 256 and 265 (calculated for $C_4F_{10}N_2$, 266). The infrared absorption spectrum of this fraction confirmed that this material was $(CF_3)_2NCF{=}NCF_3$[17] and a small amount of $CF_2{=}NCF_3$. The conversion was therefore 76.6 per cent, and the yield of dimer 100 per cent.

Reaction of $CF_2{=}NCF_3$ and NF_3

a. The reactor tube was packed with CsF and heated to 520°. A flow of dry nitrogen purged the tube and the entire system for several hours. The temperature was then lowered to 340°. The flow of azomethine and nitrogen trifluoride was then started and adjusted to a predetermined flow rate. In four hours 17 grams (0.13 moles) of $CF_2{=}NCF_3$ and 15 grams (0.21 moles) of NF_3 passed into the reactor tube. The contact time of the gas mixture was 54.5 seconds.

The products were separated by boiling into three fractions:

	Fraction	Grams
1.	lower than -70°	15
2.	-70° to 0°	9
3.	0° to +40°	8

Fraction 1 had a molecular weight range of 72 to 81. The infrared absorption spectrum was that of NF_3.

Fraction 2 was determined by infrared absorption spectroscopy, vapor phase chromatography and molecular weight to have been 1 per cent NF_3, 88 per cent $CF_2=NCF_3$ and 11 per cent $(CF_3)_2NCF=NCF_3$.

Fraction 3 was determined by infrared absorption spectroscopy, vapor phase chromatography and molecular weight to have been 100 per cent $(CF_3)_2NCF=NCF_3$.

The material balance indicated that no NF_3 had been consumed. The conversion was 50 per cent and the yield of dimer was 100 per cent.

b. The reaction of NF_3 and $CF_2=NCF_3$ over CsF was repeated at 450°. The contact time of the gas mixture was 30.5 seconds. The same separation and identification techniques were employed. NF_3 was not consumed in the reaction. The conversion to products was 65 per cent and the yield of dimer 100 per cent.

c. The reaction of NF_3 and azomethine was attempted at 620°. The reactor was evacuated and heated to 620° for 18 hours. The system was then brought to atmospheric pressure with dry nitrogen, and purged until the reaction was started. The $CF_2=NCF_3$, NF_3 mixture produced colored

products, so an attempt was made to purge the system with NF_3. At a contact time of circa 100 seconds, the colored products persisted for over 24 hours. The attempt to react NF_3 with azomethine at 620° was abandoned.

d. The system was purged with dry nitrogen at 620° for 18 hours. The temperature was then reduced to 537°. Over a period of 20.33 hours, 38 grams (0.536 moles) of NF_3 and 90 grams (0.676 moles) of CF_2=NCF_3 were allowed to enter the reactor. The calculated residence time of the gas mixture was 31.6 seconds. Products were collected in a Dry Ice-cooled trap and a liquid air-cooled trap in series. When the reaction was completed, the liquid air-cooled trap contained 36 grams and the Dry Ice-cooled trap 92 grams.

The lower-boiling fraction was transferred into a vacuum system and molecular weights and infrared absorption spectra were taken. The first 0.2 grams had a molecular weight of 73. The infrared absorption spectra indicated that this material was the NF_3 starting material.

The products collected in the Dry Ice-cooled trap were fractionated in a vapor take-off column with the following results:

Fraction	Grams	Molecular Weight
1. overhead	7.0	77 to 109
2. -56.0° to -55.2°	1.3	
3. -55.2° to -50.0°	1.4	
4. -50.0° to -39.0°	3.3	
5. -39.0° to -36.0°	1.1	
6. -36.0° to -34.0°	4.4	128.0
7. -34.0° to -31.4°	20.0	133.0
8. -31.4° to -28.0°	18.4	132.1
9. -28.0° to -11.0°	1.0	
10. -11.0° to +26.0°	3.5	
	61.4	

Fraction 6 was determined by molecular weight, infrared absorption spectroscopy and vapor phase chromatography to be 4.3 grams of CF_2=NCF_3. Fraction 7 was pure CF_2=NCF_3, and fraction 8 was over 99 per cent CF_2=NCF_3. The amount of CF_2=NCF_3 that was returned unreacted was 42.7 grams (0.322 moles).

The pot residue of the low-boiling fractionation was in turn fractionated on a liquid take-off column with the following results:

Fraction	Grams	Molecular Weight
1. overhead	4.1	269
2. 31.0° to 32.5°	5.0	295
3. 32.5° to 34.5°	4.1	291
4. 34.5° to 36.5°	4.0	277
5. 36.5° to 37.5°	4.5	269
6. pot residue	4.0	267
	25.7	

The individual fractions were examined by infrared absorption spectroscopy as well as by vapor phase chromatography, and all fractions were found to be mixtures of the known compounds $(CF_3)_2NCF{=}NCF_3$ and $(CF_3)_2NN(CF_3)_2$.[16,17] The relative amount of each was calculated from a series of molecular weights and was consistent with the chromatographic analyses.

Fraction	Grams	Grams of $(CF_3)_2NN(CF_3)_2$	Grams of $(CF_3)_2NCF{=}NCF_3$
1. overhead	4.1	3.0	
2. 31.0° to 32.5°	5.0	4.6	0.4
3. 32.5° to 34.5°	4.1	2.6	1.5
4. 34.5° to 36.5°	4.0	1.2	2.8
5. 36.5° to 37.5°	4.5	0.4	4.1
6. pot residue	4.0	0.1	3.9
		11.9 (0.039 moles)	12.7 (0.048 moles)

Of the original 90.0 grams (0.68 moles) of CF_2=NCF_3, 42.7 grams were recovered, or 47.3 grams (0.36 moles) were converted to products. The conversion to products was 47 per cent. The conversion to tetramethylhydrazine required two moles of azomethine. The yield was therefore 25 per cent. The conversion to the dimer also required two moles of azomethine and the yield was 31.3 per cent.

Reactions of C_3F_6 over Cesium Fluoride

The flow reaction of C_3F_6 over CsF

A cylinder containing C_3F_6 was connected through a flow meter to a heated reactor tube containing CsF. The products were collected in a Dry Ice-cooled trap, which was vented to the atmosphere through a drying tube. A quantity of 25.0 grams (0.167 moles) of C_3F_6 was passed through the reactor. The reactor temperature was 350°, and the contact time was circa 123 seconds. A simple bulb-to-bulb distillation yielded 1.1 grams (0.0036 moles) of material boiling higher than 30°. The conversion to products was therefore 4.3 per cent.

The remaining low-boiling material was then allowed to warm slowly and pass through the reactor tube, leaving behind anything that boiled above room temperature, and the trap containing the higher-boiling material was removed.

A fresh trap was inserted, and the material on the other side of the reactor tube was allowed to warm, forcing the low-boiling material back through the reactor tube, and once again leaving the higher-boiling material behind. This process was repeated 14 times. A bulb-to-bulb distillation yielded 15.3 grams of material boiling below room temperature. The molecular weights of this material were taken as it was transferred. The molecular weight of the first 0.3 grams was 147 and of the last 0.3 grams was 153.

The higher-boiling material contained some C_3F_6. The products in this fraction were separated chromatographically at room temperature on an eleven meter column packed with hexadecane. The products were:

Chromatographic Fraction	Grams
1.	1.8
2.	0.1
3.	0.5
4.	3.0
5.	3.8

Fraction 1 contained C_3F_6 and all intercuts.

Fraction 2 contained a very small amount of a

material which, from its infrared absorption spectrum, appeared to be $(CF_3)_2CFC(CF_3)=CF_2$. This was not a known compound, and there was an insufficient amount of material for characterization.

Fraction 3 had a molecular weight of 299. The infrared absorption and NMR spectra (see Table II) gave very strong evidence for the structure $(CF_3)_2CFCF=CFCF_3$.

Fraction 4 had a molecular weight of 299. The infrared absorption spectrum indicated that this material had been previously prepared.[10] The NMR spectrum (see Table II) indicated that the material was definitely $(CF_3)_2C=CFCF_2CF_3$.

Fraction 5 had a molecular weight of 341. The infrared absorption spectrum indicated that this was an impure sample (about 3 per cent impurity) of $(CF_3)_2CFCF(CF_3)_2$. This compound had been previously reported.[10] The compound boiled at 54.7 to 55.1°. The NMR spectrum confirmed this structure (see Table II).

A total of 7.9 grams (0.0526 moles) of C_3F_6 was consumed in the reaction. The yield of dimers was:

Fraction	Grams	Moles	Yield-Per Cent
2.	0.1	0.0003	1.1
3.	0.5	0.0015	5.5

Fraction	Grams	Moles	Yield-per cent
4.	3.0	0.0090	33.0
5.	3.8	0.0112	42.5

The material balance did not account for 0.021 moles of C_3F_6.

The reaction of C_3F_6 over CsF in a stainless steel reactor

A 500 cc. stainless steel reaction vessel was used. Under conditions that allowed as little moisture as possible to come into contact with the CsF, 100 grams of CsF were placed in the reactor. The reactor was heated to 500° for several days. The vessel was evacuated during heating to remove any residual moisture that may have been absorbed by the CsF.

Forty-six grams of C_3F_6 were condensed in the reactor and allowed to warm to room temperature. The reactor was then slowly heated in a furnace. Pressure and temperature were recorded. The pressure was 104 psig. at 30°. After 49.5 hours, the temperature was 180° and the increase of pressure with temperature had been almost linear. In the next 17.5 hours, the temperature rose to 200°, the pressure reached a maximum of 195 psig. and then dropped to 183 psig. In the next 69.5 hours, as the

temperature was increased to 215°, the pressure decreased to 133 psig.

The reactor was cooled to room temperature. The pressure was 55 psig. The reactor was then heated to 206° for 24 hours and the final pressure at this point was 123 psig.

A simple bulb-to-bulb distillation yielded 12 grams of material that boiled below room temperature. This material was assumed to be C_3F_6. Also, there was material boiling at circa 30°. This material weighed 1.2 grams. The molecular weight of 247 indicated that this was a C_5F_{10} isomer.

The remainder of the material was analyzed by vapor phase chromatography. One material appeared at exactly the calculated appearance time for $(CF_3)_2C{=}CFCF_2CF_3$. An infrared absorption spectrum of a sample, that boiled from 49.9 to 50.1° in a fractionating column, confirmed the vapor phase chromatography analysis. This perfluorohexene-3 represented 68.4 per cent of the materials boiling above room temperature. The remainder of the material was analyzed chromatographically by checking against known C_7F_{16} isomer, C_8F_{18} isomers and C_9F_{20} isomers. The product boiling above 20° was by weight:

4.0 per cent	a C_5F_{10} isomer
68.4 per cent	a C_6F_{12} isomer
4.3 per cent	a C_7F_{14} isomer
10.0 per cent	a C_8F_{16} isomer
7.9 per cent	one C_9F_{18} isomer
4.9 per cent	another C_9F_{18} isomer
less than 0.5 per cent	a C_6F_{14} isomer

The conversion to products was 74 per cent. The mole per cent of the products was:

a C_5F_{10} isomer	3.5 per cent
$(CF_3)_2C{=}CFCF_2CF_3$	60.7 per cent
$(CF_3)_2CFCF(CF_3)_2$	0.4 per cent
a C_7F_{14} isomer	4.0 per cent
a C_8F_{16} isomer	15.0 per cent
a C_9F_{18} isomer	12.0 per cent

In carrying out the reaction and identifying the products, 4.7 grams of material were lost.

Reaction of $CF_2{=}CFCF_2CF{=}CF_2$ and NF_3

Reaction at 540°

Perfluoropentadiene-1,4 was placed in a bubbler, the temperature of which was maintained by a cold water bath

at 20°. NF_3 was stored in a cylinder and bubbled through the pentadiene in an attempt to feed equal molar quantities of the two materials into a nickel reactor tube. The temperature of the reactor was 540°. The reaction tube was packed with CsF. Over a period of 20 hours, 3.2 grams (0.015 moles) of C_5F_8 and 3.2 grams (0.045 moles) of NF_3 were passed through the reactor and collected in a liquid air trap. The products were allowed to warm to -10° at atmospheric pressure. The low-boiling material was allowed to vaporize and was collected in a liquid air trap. It was shown chromatographically and by infrared absorption analysis to be NF_3. The material remaining behind was shown chromatographically to be 78.8 per cent one material. This material had a molecular weight of 212. (calculated for C_5F_8, 212), and boiled at +3.4 to +3.6° (762 mm). The infrared absorption spectra indicated weak lines at 4.9 and 5.1 microns. This material corresponded to $CF_3C{\equiv}CCF_2CF_3$, which had previously been prepared by Henne and Latif.[18]

Reaction at 200°

A reactor packed with CsF was heated to 200° and 6 grams (0.085 moles) of NF_3 was bubbled through 4.2 grams

(0.02 moles) of pentadiene-1,4 over a period of 2.67 hours. The bulk of the low-boiling material was removed from the products, and was found to be NF_3. The higher-boiling material was analyzed chromatographically. It was 78.0 per cent $CF_3C{=}CCF_2CF_3$. There was no evidence of polymeric materials.

Reaction at 240°

A quantity of 29.1 grams (0.137 moles) of pentadiene-1,4 and 5.3 grams (0.075 moles) of NF3 was passed through the reactor in 13.3 hours. The temperature was maintained at 240°. The contact time of the gas mixture was 161 seconds.

The products were fractionated on the low-temperature column.

Fraction	Grams
1. overhead	5.8
2. 0° to +3.0°	24.6
3. +3.0° to +7.0°	1.1
4. pot residue	2.6
	34.1

Reactions of the C_5F_8 Isomers over Alkali Metal Fluorides

Perfluoropentadiene-1,4

a. The 1,4-diene was prepared from Kel-F acid 683

($CF_2ClCFClCF_2CFClCF_2COOH$) by conversion to the sodium salt, pyrolysis to $CF_2ClCFClCF_2CF=CF_2$ and subsequent dehalogenation with zinc in isopropyl alcohol.[19]

b. The reactor packed with CsF was heated to 240°, and 9.6 grams (0.0452 moles) of pentadiene-1,4 were passed through the tube in 3.6 hours. The contact time was 205 seconds. The product was collected in a liquid air trap, and an attempt was made to separate it by refluxing it off a cold head at +6.0°. Both the overhead and the material remaining in the pot gave the infrared absorption spectrum expected for $CF_3C{\equiv}C\text{-}CF_2CF_3$, so the two portions were recombined and stored for fractionation.

The yield was determined chromatographically to be 97.6 per cent $CF_3C{\equiv}CCF_2CF_3$ and traces of other isomers. The results of this experiment and all following experiments are summarized in Table III.

c. The pentadiene-1,4 was passed over CsF at 240°. The contact time was 150 seconds. The product was 98 per cent $CF_3C{\equiv}CCF_2CF_3$.

d. Pentadiene-1,4 was passed over NaF at 160°. The flow per hour was 3.6 grams, and the contact time was 160 seconds. The product was 99 per cent $CF_2{=}CFCF_2CF{=}CF_2$.

e. Pentadiene-1,4 was passed over NaF at 220°. The

contact time was 115 seconds. The products were:

96 per cent	$CF_2=CFCF_2CF=CF_2$
1 per cent	$CF_3C\equiv CCF_2CF_3$
1 per cent	$CF_3\underline{CFCF=CFCF_2}$
1 per cent	$CF_3\underline{C=CFCF_2CF_2}$
1 per cent	$CF_2=CFCF=CFCF_3$

f. Pentadiene-1,4 was passed over NaF at 440°. At a contact time of 213 seconds the products were:

58 per cent	$CF_3\underline{C=CFCF_2CF_2}$
27 per cent	$CF_3C\equiv CCF_2CF_3$
10 per cent	$\underline{CF_2CF=CFCF_2CF_2}$
5 per cent	$CF_2=CFCF_2CF=CF_2$

g. Pentadiene-1,4 was passed over NaF at 440°. The contact time was 100 seconds. The products were:

55 per cent	$CF_3\underline{C=CFCF_2CF_2}$
35 per cent	$CF_3C\equiv CCF_2CF_3$
5 per cent	$CF_2=CFCF_2CF=CF_2$
4 per cent	$\underline{CF_2CF=CFCF_2CF_2}$
0.5 per cent	$CF_2=CFCF=CFCF_3$
0.5 per cent	$CF_3\underline{CFCF=CFCF_2}$

h. Pentadiene-1,4 was passed over granular carbon at 440°. The contact time was calculated to be 370 seconds.

The products were:

40 per cent	$CF_2=CFCF_2CF=CF_2$
40 per cent	$CF_2=CFCF=CFCF_3$
20 per cent	$CF_3C\equiv CCF_2CF_3$

i. Pentadiene-1,4 was passed over NaF pellets that had been impregnated with carbon. The reactor was heated to 240°. The contact time is not known exactly, but was between 150 and 175 seconds. The product was 97 per cent $CF_2=CFCF_2CF=CF_2$.

j. Pentadiene-1,4 was passed over the above-mentioned C-NaF pellets at 340°. The contact time was 213 seconds. The products were:

65 per cent	$CF_2CF=CFCF_2CF_2$
20 per cent	$CF_3C=CFCF_2CF_2$
10 per cent	$CF_2=CFCF=CFCF_3$
5 per cent	$CF_3CFCF=CFCF_2$

k. Pentadiene-1,4 was passed over C-NaF pellets at 440°. The contact time was 124 seconds. The products were:

50 per cent	$CF_2CF=CFCF_2CF_2$
40 per cent	$CF_3C=CFCF_2CF_2$
5 per cent	$CF_2=CFCF=CFCF_3$
3 per cent	$CF_2=CFCF_2CF=CF_2$

1. A sample of pentadiene-1,4 was placed in a heavy-walled glass ampule and heated to 360° for 72 hours. The maximum pressure was calculated by the Ideal Gas Law to be 10.7 atmospheres. Chromatographic examination indicated that the product was:

94 per cent	$CF_2=CFCF_2CF=CF_2$
4 per cent	$CF_2=CFCF=CFCF_3$
2 per cent	$CF_3C\equiv CCF_2CF_3$

m. A heavy-walled glass ampule was loaded with 10.5 grams of pentadiene-1,4 and subjected to 10^7 roentgens of gamma radiation from a Co^{60} source. Less than 0.5 grams of a brown soupy polymer formed. The remainder of the product was:

98 per cent	$CF_2=CFCF_2CF=CF_2$
2 per cent	$CF_2=CFCF=CFCF_3$

Perfluoropentyne-2

a. All previously-produced quantities of $CF_3C=CCF_2CF_3$ were combined. Some had been fractionated, and some merely had the low-boiling material stripped off. The fractionation gave the following data:

Fraction	Grams
1. overhead	3.7
2. -3.5° to 0°	1.3
3. 0° to +2.0°	2.4
4. +2.0° to +4.1°	97.6
5. +4.1° to +7.5°	3.1
6. pot residue	5.7

The material of Fraction 4 was retained for chemical and physical testing. The sample was analyzed by gas chromatography for purity. The columns were at room temperature (28°). On a two meter column packed with hexadecane, with a gauge pressure of 3 psi. and a flow of 6 arbitrary units, less than 0.1 per cent impurity was indicated. On a two meter column packed with the ester of Kel-F acid 8-11-4, with a pressure of 3 psig. and a flow of 4.7 arbitrary units, the indicated impurity was considerably less than 0.1 per cent.

The boiling point was obtained by the capillary tube method. At 762 mm. the material boiled at +3.6° and condensed at +3.3°. The molecular weight by the Dumas method was as follows:

At	198 mm.	212
	203 mm.	212
	180 mm.	212

b. A basic hydrolysis of the pentyne-2 was attempted. A heavy-walled glass ampule was loaded with 6.2 grams of pentyne-2 and an excess of a 50 per cent NaOH solution. The ampule was heated to 75° for 25 hours. Upon opening the tube, 6.2 grams of material having a molecular weight of 212.0 and having an infrared absorption spectrum of pentyne-2 were recovered.

The pentyne-2 (3 grams) was sealed in an ampule with a 3 molar KI solution. The ampule was heated for 48 hours to a temperature of 90°. Very little iodine was formed. The ampule was opened, and the gaseous products removed and dried. The infrared absorption spectrum of the product was essentially that of the starting material.

c. A heavy-walled glass ampule, 2.5 by 11 cm., was loaded with 22.0 grams of $CF_3C{\equiv}CCF_2CF_3$. The lower half of the ampule was heated to 360° for 72 hours. The tube was then cooled and the products removed. Except for the formation of a very small amount of tar, the pentyne-2 was returned unreacted. The pentyne-2 was identified by its infrared absorption spectrum. It showed no impurities on chromatographic analysis.

d. A heavy-walled glass ampule was loaded with 6.0 grams of $CF_3C{\equiv}CCF_2CF_3$ and subjected to 2.7×10^7 roentgens of gamma radiation from a Co^{60} source. A white polymer formed. The pentyne-2 did not completely polymerize, as 3.1 grams of liquid remained. The liquid was identified by infrared absorption spectroscopy to be pure pentyne-2. The polymer was insoluble in many types of solvents. A powder-film of the polymer showed definite infrared absorptions, but no absorptions between 5.0 and 6.0 microns. The polymer was heated on a melting point apparatus and temperatures were observed by using a chromel-alumel thermocouple. The solid began to shrink at 428°; at 434° it had some liquid character. At this point the color began to darken until, at 458°, gas was evolved, and the liquid turned brown.

e. A quantity of 4 grams (0.018 moles) of pentyne-2 was passed over NaF at 520° in one hour. The contact time was 83 seconds.

The products were examined chromatographically and were:

92 per cent	$CF_3C{\equiv}CCF_2CF_3$
4 per cent	$CF_3\underline{C{=}CFCF_2}CF_2$
4 per cent	$\underline{CF_2CF_2CF_2CF{=}CF}$

f. A quantity of 7.3 grams of pentyne-2 at a flow rate of 3.4 grams (0.016 moles) per hour was passed over CsF at 520°. The contact time was 118 seconds. The products were:

40 per cent	$CF_3C{\equiv}CCF_2CF_3$
30 per cent	$CF_3\underline{C=CFCF_2}CF_2$
20 per cent	$CF_2=CFCF_2CF=CF_2$
10 per cent	$CF_2=CFCF=CFCF_3$

g. A quantity of 2.3 grams of pentyne-2 at a flow rate of 3.4 grams (0.016 moles) per hour was passed over CsF at 440°. The contact time was 114 seconds. The products were:

88 per cent	$CF_3C{\equiv}CCF_2CF_3$
3 per cent	$CF_3\underline{CFCF=CFCF_2}$
3 per cent	$CF_3\underline{C=CFCF_2}CF_2$
3 per cent	$CF_2=CFCF=CFCF_3$
3 per cent	$CF_2=CFCF_2CF=CF_2$

h. A quantity of 3.6 grams of pentyne-2 was passed over CsF at a flow rate of 3.6 grams (0.017 moles) per hour. The temperature was 240°, and the contact time 150 seconds. The product was 100 per cent $CF_3C{\equiv}CCF_2CF_3$.

i. A quantity of 3.5 grams (0.0165 moles) of pentyne-2 was passed over NaF at 440° in one hour. The

contact time was 137 seconds. The products were:

99.5 per cent	$CF_3C{\equiv}CCF_2CF_3$
0.5 per cent	$CF_2{=}CFCF{=}CFCF_3$

j. A quantity of 4.0 grams of pentyne-2 at 3.0 grams (0.014 moles) per hour was passed over granular carbon at 440°. The contact time was 137 seconds. The product was 99 per cent $CF_3C{\equiv}CCF_2CF_3$.

Perfluorocyclopentene

a. This isomer was produced in good yields when pentadiene-1,4 was passed over C-NaF pellets at 340°. In order to produce a large quantity of material (for further experiments and to confirm the cyclopentene structure) a different synthetic route was employed.

An available sample of $CF_2CF_2CF_2CCl{=}CCl$ was utilized to synthesize $CF_2CF_2CF_2CF{=}CF$. Thirty grams of CoF_3 was placed in a one liter flask equipped with a stirrer, dropping funnel and a reflux condenser. A quantity of 122 grams of the $C_5F_6Cl_2$ was allowed to drip into the flask. The temperature of the flask was increased until a good reflux rate was observed. The temperature of the refluxate rose from 85 to 87° over a 37 hour period. The products were fractionated. A fraction boiling at 82.5 to 84.5° was examined by infrared absorption spectro-

scopy, refractive index and vapor phase chromatography. All the properties indicated that the product was a mixture of about 60 per cent cyclo-$C_5F_8Cl_2$ and 40 per cent cyclo-$C_5F_6Cl_2$. The mixture was dehalogenated with zinc, using dry isopropyl alcohol as a solvent. By using a water condenser, only $\underline{CF_2CF_2CF_2CF{=}CF}$ and a small amount of alcohol were collected in a Dry Ice trap. Passing the more volatile fraction through P_2O_5 removed all impurities, and a pure sample of perfluorocyclopentene remained. The yield was 64 grams or 61.0 mole per cent of the starting material. No attempt was made to recover unfluorinated cyclo-$C_5F_6Cl_2$.

Perfluorocyclopentene had a characteristic infrared absorption of 5.70 microns, boiled at 29.0 to 29.4° and gave the expected NMR spectra (see Table II). This compound was reported by Henne and Latif.[18]

b. A sample of cyclopentene was passed over CsF at 240°. The flow rate was 3.75 grams (0.0179 moles) per hour. The contact time was 100 seconds. The product was 100 per cent cyclopentene.

c. The reactor was packed with NaF and heated to 340°; cyclopentene was allowed to enter the tube at a rate of 3.4 grams (0.016 moles) per hour. The contact time

was 140 seconds. The product was 100 per cent cyclopentene.

d. The reactor was packed with NaF and heated to 440°; 4.8 grams of cyclopentene was allowed to enter the tube at a rate of 3.7 grams (0.0175 moles) per hour. The contact time was 115 seconds. The product was 100 per cent cyclopentene.

e. The reactor was packed with NaF and heated to 520°; 5.1 grams of cyclopentene was allowed to enter the tube at a flow rate of 3.9 grams (0.018 moles) per hour. The contact time was 88 seconds. The products were:

97 per cent	$\underline{CF_2CF_2CF_2CF{=}CF}$
2 per cent	$CF_2{=}CFCF{=}CFCF_3$
1 per cent	$CF_3C{\equiv}CCF_2CF_3$

f. A heavy-walled glass ampule was loaded with 12 grams of cyclopentene. The total pressure at 360° was calculated by the Ideal Gas Law to be 11 atmospheres. The ampule was sealed and heated to 360° for 72 hours. The ampule was opened directly into the vacuum system. The products were:

99.5 per cent	$\underline{CF_2CF_2CF_2CF{=}CF}$
0.5 per cent	$CF_3\underline{C{=}CFCF_2}CF_2$

g. A heavy-walled glass ampule was loaded with 10.6 grams of cyclopentene, sealed and subjected to 10^7 roentgens

of gamma radiation by a Co^{60} source. The product was 100 per cent cyclopentene.

Perfluoromethylcyclobutene-1

a. This isomer was prepared in 55 per cent yield by passing perfluoropentadiene-1,4 over NaF at 440°. The isomers, however, could not be separated by distillation, so it was necessary to separate several gram quantities by chromatographic methods. An eleven meter column at room temperature packed with hexadecane was used in each case.

In a typical run, 30 grams of pentadiene-1,4 was passed over NaF at 440° in 14 hours. The flow was 2.1 grams (0.01 moles) per hour, and the contact time was 213 seconds. A total of 29.2 grams of product was collected in the liquid air-cooled trap. Of the 29.2 grams, 4 grams were polymeric. The remaining 25.2 grams were separated chromatographically to give:

14.0 grams	methylcyclobutene-1
6.5 grams	pentyne-2
2.3 grams	cyclopentene
1.3 grams	pentadiene-1,4
24.1	

The remaining 1.1 grams were intercuts.

b. The characteristic C=C absorption in the infrared spectrum of this isomer was at 5.77 ± 0.2 microns. The infrared absorption spectrum suggested the cyclobutene structure (see Table I).

The NMR spectrum indicated that there was one CF_3 group, two CF_2 groups and one CF group (see Table II).

The molecular weight of this material was 212.0 and the elemental analysis indicated 28.14 per cent C (calculated 28.30 per cent C) and 71.86 per cent F (calculated 71.70 per cent F). The material boiled at +11.9° and condensed at +11.0° as determined by the capillary method.

A flask was fitted with a Dry Ice-cooled condenser. To an excess of $KMnO_4$ in frozen acetone, 7 grams of methylcyclobutene-1 were added. The condenser was packed with Dry Ice and the mixture was allowed to warm slowly. An exothermic reaction occurred. Heat was cautiously added until it was evident that methylcyclobutene-1 was no longer refluxing. The material was filtered and acidified with H_2SO_4. As H_2SO_4 was added, the acetone polymerized, so water was added and the insoluble material was filtered out. The keto-acid was extracted with ethyl ether. Most of the ether was evaporated and the remaining liquid was distilled. The fraction boiling at 134 to 137°

weighed 4.7 grams. An NMR spectrum of this sample indicated the presence of one CF_3 group and two CF_2 groups (see Table II). This fraction was believed to be the oxidation product of methylcyclobutene-1, $CF_3COCF_2CF_2COOH$, or a hydrated form of the keto-acid. The product formed a crystalline solid with phenylhydrazine by standard organic techniques generally employed to prepare hydrazones from ketones. The crystals melted sharply at 149.6 to 150.0°. The infrared absorption spectrum of the keto-acid indicated two different $-\overset{O}{\overset{\|}{C}}-$'s, an OH and C-F absorptions. A basic hydrolysis of the acid was conducted potentiometrically. Two end points were observed - one at pH2 and one at pH8. The titration of the material as distilled gave a molecular weight of 274.1 (calculated $CF_3COCF_2CF_2COOH$, 242, $CF_3C(OH)_2CF_2CF_2COOH$, 260). The remaining acid was placed on a dessicator with P_2O_5. After a few days the titration was repeated, and a molecular weight of 266 was obtained.

c. A quantity of 2.1 grams of methylcyclobutene-1 was passed over CsF at the rate of 2.8 grams (0.0132 moles) per hour. The contact time was 200 seconds. The reactor was heated to 240°. The products were:

97 per cent	$CF_3\underline{C=CFCF_2CF_2}$
2 per cent	$CF_2=CFCF=CFCF_3$

1 per cent $CF_3C{\equiv}CCF_2CF_3$

d. Methylcyclobutene-1 was passed over NaF at 440°. The flow was 2.9 grams (0.0137 moles) per hour, and the contact time was 130 seconds. The products were:

85 per cent $CF_3\underline{C{=}CFCF_2CF_2}$

9 per cent $CF_3C{\equiv}CCF_2CF_3$

3 per cent $\underline{CF_2CF_2CF_2CF{=}CF}$

3 per cent $CF_2{=}CFCF_2CF{=}CF_2$

e. A heavy-walled glass ampule was loaded with 2.1 grams of methylcyclobutene-1 and sealed. The ampule was heated to 360°. Black polymeric material began forming immediately, but the heating was continued for 72 hours. The ampule was cooled and opened. The liquid remaining weighed 1.2 grams and had the following composition:

91 per cent $CF_3\underline{C{=}CFCF_2CF_2}$

6 per cent $CF_2{=}CFCF{=}CFCF_3$

3 per cent $CF_3C{\equiv}CCF_2CF_3$

f. A heavy-walled glass ampule was loaded with 7.5 grams of methylcyclobutene-1 and subjected to 10^7 roentgens of gamma radiation by a Co^{60} source. The products were:

99.9 per cent	$CF_3C{=}CFCF_2CF_2$
0.1 per cent	$CF_3C{\equiv}CCF_2CF_3$

Perfluoropentadiene-1,3

a. This isomer was produced in many of the reactions with C_5F_8 isomers. An independent method of preparation was sought to aid in the characterization of the isomer and to make available sufficient quantities for further experiments.

The reactor was packed with CsF and heated to 240°. One end of the tube was connected to a trap which was cooled to -185° by liquid air. The other end of the tube was connected to a flask, insulated with glass wool and warmed with a heating mantle. In the flask were placed 28.8 grams of $CF_2ClCFClCF_2CF{=}CF_2$ (boiling point 90°). The flask was heated above the boiling point of the olefin, and the olefin was vaporized into the heated reactor. The products were collected in the liquid air-cooled trap. The entire 28.8 grams were transferred in 45 minutes. The system was then evacuated through the trap so that no material remained in the system. The liquid was fractionated to obtain 19.0 grams of material boiling from 73.5 to 75.0°, $n_D^{20.5} = 1.3298$. This olefin was dehalogenated by

a standard method to give 13.6 grams of a material which, after drying in P_2O_5, had a molecular weight of 212, an elemental analysis of 28.32 per cent C (calculated 28.30 per cent C for C_5F_8) and 71.64 per cent F (calculated 71.70 per cent F for C_5F_8). This material boiled at 26.9° and condensed at 26.3°. The C=C absorptions in the infrared spectrum appeared at 5.82 and 5.58 microns (see Table I). The NMR spectrum of this isomer indicated three CF groups (two similar), one CF_2 group and one CF_3 group (see Table II). This synthesized material had exactly the same infrared absorption spectrum as the material prepared in several of the isomerizations of the pentadiene-1,4.

b. The reactor was packed with CsF and heated to 240°; 5 grams of pentadiene-1,3 were passed through the tube at a rate of 3.75 grams (0.0177 moles) per hour. The contact time was 140 seconds. The products were:

95 per cent	$CF_3C{\equiv}CCF_2CF_3$
1 per cent	$CF_3\underline{CFCF{=}CFCF_2}$
1 per cent	$CF_3\underline{C{=}CFCF_2CF_2}$
1 per cent	$CF_2{=}CFCF{-}CFCF_3$
1 per cent	$\underline{CF_2CF_2CF_2CF{=}CF}$
1 per cent	$CF_2{=}CFCF_2CF{=}CF_2$

c. The reactor was packed with NaF and heated to 320°; pentadiene-1,3 was passed through the tube at the rate of 3.6 grams (0.0169 moles) per hour. The contact time was 125 seconds. The products were:

60 per cent	$CF_3C{\equiv}CCF_2CF_3$
24.8 per cent	$CF_3\underbrace{C{=}CFCF_2CF_2}$
15.2 per cent	$CF_2{=}CFCF{=}CFCF_3$

d. The reactor was packed with NaF and heated to 440°; pentadiene-1,3 was passed through the tube at 4 grams (0.0188 moles) per hour. The contact time was 98 seconds. The products were:

60 per cent	$CF_3C{\equiv}CCF_2CF_3$
40 per cent	$CF_3\underbrace{C{=}CFCF_2CF_2}$

e. A heavy-walled glass ampule was loaded with 2.5 grams of pentadiene-1,3. The tube was sealed and heated to 360° for 72 hours. The maximum pressure was calculated by the Ideal Gas Law to be 10.7 atmospheres.

The ampule was cooled and opened directly into the vacuum system. It contained 1.3 grams of higher-boiling material and 1.2 grams of material boiling below room temperature. The volatile products were:

60 per cent	$CF_2{=}CFCF{=}CFCF_3$
25 per cent	$\underbrace{CF_2CF_2CF_2CF{=}CF}$
10 per cent	$CF_3C{\equiv}CCF_2CF_3$

3 per cent	$CF_2=CFCF_2CF=CF_2$
2 per cent	Unknown

f. A heavy-walled glass ampule was loaded with 3.1 grams of pentadiene-1,3, sealed and subjected to 10^7 roentgens of gamma radiation from a Co^{60} source. The ampule was cooled and opened into a vacuum system. The product was 100 per cent $CF_2=CFCF=CFCF_3$.

Table I

Infrared Absorption Spectra*

Perfluorocyclopentene				
5.70 m.	7.75 m.	8.52 v.s.	8.78 m.	9.95 v.s.
7.21 v.s.	8.25 s.	8.60 s.	9.10 w.	10.18 v.s.
7.49 m.				
Perfluoropentyne-2				
4.90 v.w.	7.45 m.	8.30 s.	9.02 w.	11.21 m.
5.04 v.v.w.	7.87 v.s.	8.41 v.s.	9.39 v.s.	14.59 s.
6.55 to 6.95 (unresolved)	8.10 v.s.	8.62 s.	9.81 w.	
Perfluoropentadiene-1,4				
5.61 v.s.	7.77 s.	8.40 v.s.	9.40 m.	10.85 s.
7.39 v.s.	8.20 w.	8.81 m.	9.56 s.	11.15 v.s.
7.60 v.s.				
Perfluoromethylcyclobutene-1				
5.77 s.	7.40 s.	7.99 m.	8.40 v.s.	10.29 s.
6.85 v.w.	7.51 v.s.	8.12 m.	8.65 m.	11.50 s.
6.95 w.	7.84 v.s.			
Perfluoropentadiene-1,3				
5.59 s.	6.88 w.	7.90 s.	8.93 s.	11.03 v.s.
5.77 w.	7.17 v.s.	8.25 v.s.	9.35 s.	13.57 s.
6.20 w.	7.50 v.s.	8.66 s.	10.39 s.	
4,5-Dichlorooctafluoropentene-1				
5.60 s.	7.97 m.	8.92 s.	10.76 m.	12.10 s.
7.20 m.	8.19 s.	9.39 s.	10.95 m.	12.39 s.
7.35 s.	8.40 v.s.	10.05 s.	11.20 s.	13.16 s.
7.60 s.	8.55 v.s.	10.55 m.	11.90 s.	14.50 m.
4,5-Dichlorooctafluoropentene-2				
5.86 w.	8.20 s.	9.45 m.	11.19 m.	13.17 m.
7.19 s.	8.49 v.s.	9.81 m.	12.06 s.	14.49 m.
7.45 m.	8.79 s.	9.99 m.	12.45 m.	14.81 m.
7.99 v.s.	9.20 s.	10.51 m.	12.80 m.	

*All absorptions are reported in wavelengths (microns). The relative per cent absorption at each wavelength are described by the symbols: v. is very; w. is weak; m. is medium; and s is strong.

Table II

Nuclear Magnetic Resonance (NMR) Spectra

Compound and Peak Assignments	Peak	Chemical Shift (ppm.)	Area Ratio	Fine Structure
CF_3-CF=CF-CF=CF_2	a.	-6.3	3	Doublet
a. b. c. d. e,f.	b.	+81.0	1	Quartet
	c.	+81.0	1	Quartet
	d.	+113.0	1	Doublet
	e.	+16.8	1	Doublet
	f.	+29.2	1	Doublet
CF_3-CF_2C=C-CF_3	a.	+10.1	3.1	Triplet
a. b. a'.	b.	+29.7	3.0	Septet
	a'.	-21.2	2.8	Triplet
CF_3-C=CF-CF_2-CF_2	a.	-16.0	3.1	Doublet
a. d. b. c.	b.	+39.8	1.9	Triplet and Quartet
	c.	+23.1	1.0	Triplet
	d.	+43.5	2.0	Doublet
CF_3-C-CF_2-CF_2COOH	a.	+4.4	3	Triplet
a. b. c.	b.	+41.5	2	Quartet
	c.	+46.4	2	Multiplet
$(CF_3)_2$-CF-CF=CF-CF_3	a.	0	6	Triplet
a. e. d. c. a'.	a'.	+111.0	1	Doublet
	c,d.	+80.9	2	
	e.	-6.3	3	Doublet
(CF_3) C=CF-CF_2-CF_3	a.	-20.9	2.9	Complex
(CF_3) a.	a'.	-17.5	2.9	Doublet
	a''.	+7.35	2.9	Complex
a'. c. b. a''.	b.	+44.7	2.0	Complex
	c.	+22.4	1.0	Complex
$(CF_3)_2$CFCF$(CF_3)_2$	a.	-5.3	6	Doublet
a. b.b. a.	b.	+103.2	1	Multiplet

DISCUSSION

The Synthesis of N_2F_4

Dinitrogentetrafluoride had been reported as a product of a reaction between NF_3 and certain solid metals.[20] When copper was used, temperatures near 375° and residence times in the order of 13 minutes* were required for reaction. It appeared that as the reaction proceeded, a protective copper fluoride coating was formed, which necessitated increasing the apparent reaction temperature and/or residence times with a corresponding decrease in the yield of N_2F_4. It has also been reported that N_2F_4 has been prepared in small yields by the vapor phase fluorination of ammonia.[21] An arc discharge process reported by Frazer[22] converts NF_3 to N_2F_4 and N_2F_2 in the presence of mercury in substantial (51 to 67 per cent) yields, but the process

*There appears to be a typographical error in Colburn's paper. Dr. Colburn has stated that the contact time was 13 seconds.

was operated at 1 to 4 mm. pressure and the production rate was slow.

In an attempt to find a suitable laboratory scale preparation of N_2F_4, NF_3 was found to react successfully with mercury in a flow system at between 320 to 330°.[23] Temperatures outside this range tended to lower the amount of desired product formed. For optimum results certain precautions, cited below, were necessary.

The reagents must be absolutely dry and free of impurities, especially oxygen-bearing substances. The NF_3 used in this work was prepared by the action of a D.C. current on a solution of pyridine in HF (Simons process). It was thoroughly scrubbed with aqueous solutions of KOH and KI and dried preliminarily with concentrated H_2SO_4. It was further dried by passage and repassage through powdered P_2O_5. Finally, it was thoroughly degassed. The mercury was redistilled to insure its purity.

The reaction system began with a cylinder of NF_3. This had a needle valve which controlled the flow of gas through a flow meter into a metal vessel containing the mercury. This vessel consisted of two sections. The lower section was made from 1 inch forged steel pipe 61 cm. long. It had a flange at the top end. Just below

the flange, on the outside of the pipe, were soldered several coils of copper tubing through which cooling water was passed. The upper section was constructed of 1 inch nickel pipe with a flange at the bottom. Through the top of this section was welded a 0.79 cm. nickel delivery tube and a like exit tube. When the two sections were assembled about a rubber gasket, the delivery tube reached to within 0.6 cm. of the bottom of the vessel. The outlet tube was attached to a glass trap in which the products were collected.

The reactor was heated with a fibrous glass heating tape wound about the lower 15 cm. of the vessel. The reaction temperatures were determined by a thermocouple which was silver soldered to the vessel about 9 cm. from the bottom.

This system, when assembled with the mercury in the reactor, was flushed with dried helium gas as the reactor was heated to 320° over a several hour period. A flow of NF_3 was then maintained, without a carrier gas, at a rate of about 8 grams per hour. As the reaction began, a sudden rise in temperature was observed. A compensation was made for this until thermal equilibrium was reached. At the end of the reaction period, the products were purged from the system with dry helium gas

into the glass collection trap which was cooled with liquid air. The outlet arm of the glass trap had a tee through which a counter flow of dry helium gas was maintained to prevent atmospheric air and water from diffusing into the system. The reaction products were transferred *in vacuo* to the pot of a low temperature fractionating column. The head of the column was cooled with liquid air and a distillation was performed under an atmosphere of helium. The mixture of N_2F_4, N_2F_2, and NF_3 was allowed to warm slowly until liquid reflux was observed. This first condensate was slowly removed *via* a stop cock to a vacuum system and recondensed. As the least-volatile component, N_2F_4, appeared in the reflux, it solidified on the head and was retained there. Finally, when no further liquid reflux was in evidence, and the pot was empty, the solidified product was transferred to another collector in the vacuum system. It was a fluffy white solid which melted to a clear, water-white liquid. It had a molecular weight of 103 to 105 and its infrared absorption spectrum was that reported for N_2F_4.[14]

If the first condensate fraction was slowly transferred *in vacuo* until a portion poor in NF_3 was retained, the residue was found to contain an undetermined amount of the so-called *cis* N_2F_2 on the basis of an infrared

absorption spectrum. This latter mixture of NF_3 and N_2F_2 was found to react with mercury and glass at room temperature. If a portion of the mixture was sealed in vacuo with some glass fragments, the reaction produced a white solid, and ultimately all the N_2F_2 was removed. On standing, the white solid that was produced slowly decomposed and evolved a brown gas with the properties of NO_2.

In a representative reaction between mercury and NF_3, using the conditions and precautions cited, 50 grams of NF_3 were reacted with an initial charge of 616 grams of Hg (48.5 ml.). Essentially 14 grams of NF_3 were recovered and 16 grams of N_2F_4 were isolated. Sixty per cent of the NF_3 that reacted was converted to N_2F_4 and to a small amount of the cis isomer of N_2F_2. The use of mercury as a reagent seems to have the following advantages over a solid metallic reagent: the metal fluoride formed, Hg_2F_2, is less dense than and insoluble in mercury; gaseous NF_3 can be bubbled through the liquid phase; the residence time is lowered to about 30 to 60 seconds; the reaction is more homogeneous.

This synthesis had several advantages over other methods. The equipment was simpler and the production

higher than the arc-discharge method. The variables were easier to control than the copper-NF_3 reaction, and less impurities were produced. The fluidized bed reaction of NF_3 and carbon[24] was difficult to control and produced C_2F_6 as an impurity. The thermal reaction of mercury and NF_3 produced only cis N_2F_2 as an impurity and the chemical reactivity of cis N_2F_2 facilitated its removal.

Effect of Alkali Metal Fluorides on C_3F_6

Christie[9] demonstrated that alkali metal fluorides catalyze the reaction between gaseous oxygen and perfluoropropylene. Because of the strong tendency of oxygen to partake in free radical reactions, it is not surprising that the free radical mechanism proposed by Gens[4] was observed. Miller[25] studied the addition of oxygen and fluorine to $CCl_2{=}CCl_2$. The mechanism proposed was: initial attack by fluorine, then reaction with oxygen.

A study of the products in the oxidation of perfluoropropylene does not supply the necessary data to determine how perfluoropropylene is affected by alkali metal fluoride catalysts. The reactant oxygen is so vigorous in free radical attack that many products would be expected - mostly the result of cleavage and recombination. The products

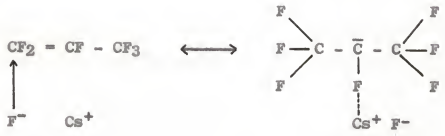
isolated by Christie[9] were COF_2, CF_3COF, $CF_3COCF_2CF_3$, CF_3COCF_3, CF_3OCF_2COF and $(CF_3)_2CFCOCF_2CF_3$.

However, Christie did add oxygen to a fluorocarbon to obtain some new, and some interesting compounds. He was able to produce all these products in good yields at 500° using NaF as a catalyst, and at 300° using CsF as a catalyst. The activity was not observed to be a surface area limited process because minor variations on contact time did not affect the conversion.

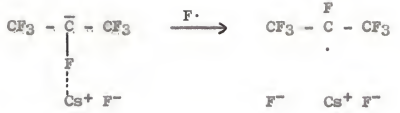
Earlier work in this laboratory[10] compared the catalytic effect of NaF and CsF on the addition of NF_3 to C_3F_6. Using NaF as a catalyst, little reaction occurred at 450°, but at 520° there was 87 per cent conversion to products. The products were CF_4, C_2F_6, $CF_2{=}NCF_3$, C_3F_8, iso C_4F_8, iso C_4F_{10}, iso C_5F_{10}, iso C_6F_{14}, $(CF_3)_2CFCF(CF_3)_2$ and $CF_3CF{=}NCF_3$.

It will be shown later in this paper that the alkali metal fluorides always isomerize olefins to lower energy structures. The wavelength of the C=C infrared absorption invariably increases in an alkali metal fluoride-induced isomerization. However, shifting the double bond of propylene gives an equivalent isomer of equal energy. It is believed, therefore, that alkali metal fluorides increase

the resonance by a large factor, and the probability of finding the electrons in the vicinity of the center carbon is greatly increased. The charge on the center carbon which had been considered would be increased, and that carbon-fluorine bond would be weakened. A cesium ion that is sharing its fluoride ion with a propylene molecule would have a slightly greater charge and could share the fluorine on the center carbon of propylene. Subsequent addition to the carbanion would release the fluorine ion to the positive cesium ion.

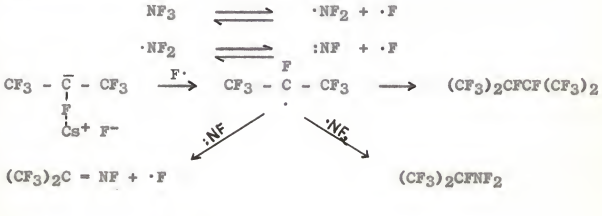


Once the carbanion is formed, it may react with a positive site on another fluorocarbon. When NF_3 is the reactant however, fluorine free radicals are present to some extent and may attack the carbanion, adding fluorine and converting the carbanion to a free radical. The free radical may then participate in further reactions.



In the reaction of NF_3 and C_3F_6 at 520° over NaF, the temperature was so high that there was carbon-carbon cleavage, creating a variety of free radicals and the possibility of a great number of products. In order to reduce the possible number of products, the reaction was attempted at a lower temperature, employing CsF as a catalyst.

The reaction between NF_3 and C_3F_6 was attempted over CsF at 320°. There was 52 per cent conversion at 320° and the products were $(CF_3)_2CFNF_2$, $(CF_3)_2C{=}NF$, $(CF_3)_2C{=}CFCF_2CF_3$ and $(CF_3)_2CFCF(CF_3)_2$. Once again the carbanion intermediate, stabilized by its association with the CsF crystal, was attacked by a fluorine atom liberated by NF_3.



A simpler attack on C_3F_6 by a fluorine radical liberated by NF_3 would explain all the products except $(CF_3)_2C{=}NF$. This product can be best explained by the carbanion mechanism. It is interesting that the fluorine atom lost upon attack of :NF on $CF_3\overset{F}{\overset{\cdot}{C}}-CF_3$ was almost quantitatively equal to the number of fluorine atoms required to produce $(CF_3)_2CFCF(CF_3)_2$.

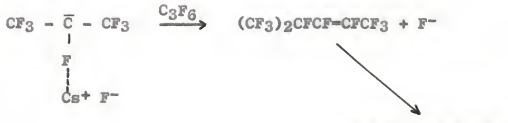
In summary, it had been demonstrated that the alkali metals catalyzed certain free radical attacks on propylene. The catalyst activity in decreasing order was: CsF, RbF, KF, NaF. By using a more active catalyst, the temperature of reaction was lowered - resulting in less fragmentation.

The issue thus far had been complicated by the nature of the material reacting with propylene. Therefore, the propylene was studied by itself in the presence of CsF. This alkali metal fluoride was chosen because it appeared to be the most active catalyst.

A few grams of CsF were placed in the bottom of a stainless steel reactor. CsF is extremely hygroscopic, so appropriate care was exercised in this operation. The reactor was fitted with a stem, a pressure gauge and a valve. The vessel was heated to 500° for several days and

evacuated to remove all residual moisture. A sample of propylene was condensed into the reactor and allowed to warm to room temperature. It was then heated slowly to 210° for several days. The pressure began decreasing at 200°. The reactor was cooled and opened into a vacuum system. Although a few grams of material were not accounted for, 12 grams of propylene were returned unreacted and 29 grams of higher-boiling material were obtained. A chromatographic analysis indicated that the higher-boiling material had the following composition: 3.5 mole per cent C_5F_{10}; 60.7 mole per cent C_6F_{12}; 0.4 mole per cent C_6F_{14}; 4.0 mole per cent C_7F_{14}; 15.0 mole per cent C_8F_{16}; 12.0 mole per cent of two C_9F_{18} isomers.

Only the two C_6's were definitely identified. They were $(CF_3)_2C{=}CFCF_2CF_3$ and $(CF_3)_2CFCF(CF_3)_2$. There was almost certain evidence of carbon-carbon bond cleavage, surprising at 210°. Employing the same mechanism that was used above:



The products were all explainable by this mechanism. If the addition of an atom of fluorine had been the initiating step, $(CF_3)_2CFCF(CF_3)_2$ would have been a major product. The very small quantity of this material that was formed precludes the initial attack of a fluorine atom as a major mechanism.

This experiment demonstrated that by using CsF, fragmentations did occur at temperatures much lower than without a catalyst[26,27,28,29] (normally above 350° in a closed reaction vessel). The absence of the product $(CF_3)_2C=C(CF_3)_2$ indicated that the carbene was probably not formed and the reactive intermediate was the carbanion. The carbanion reacted with propylene to form the hexene-2. It would be isomerized in the presence of CsF to $(CF_3)_2C=CFCF_2CF_3$. The anticipated high yield of $(CF_3)_2C=CFCF_2CF_3$ and the much lower yields of C_7's, C_8's and C_9's was exhibited. The long contact time and pressure involved, however, may have contributed to products that would not have been formed if the contact time and pressure had been lower.

A flow reactor was constructed so that the system could be studied at much lower contact times. It was anticipated that there would be a lower conversion to products because of the reduced contact time and that there would be fewer

products, making evaluation of the mechanism more valid.

A temperature of 350° was chosen because it generally requires an increase of 100° above the temperature necessary for reaction in a closed system under pressure for a reaction in a flow system. At a contact time of 123 seconds, the conversion was only 4.3 per cent. The high-boiling products were stripped off and the propylene was recycled. This procedure was repeated 15 fold.

The products were all C_6's and had to be separated chromatographically. An eleven meter column packed with hexadecane was used for this purpose. The products were:

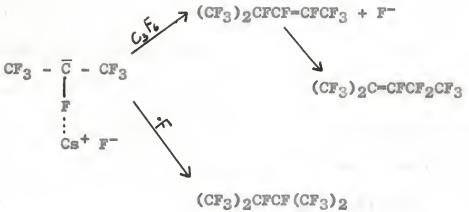
3.8 grams	$(CF_3)_2CFCF(CF_3)_2$
3.0 grams	$(CF_3)_2C{=}CFCF_2CF_3$
0.5 grams	$(CF_3)_2CFCF{=}CFCF_3$

0.1 grams believed to be $(CF_3)_2CFC(CF_3){=}CF_2$

The appearance of tetramethylethane suggested that propylene was being degraded to carbon and fluorine because no other fragmentation products were found. The large number of steps in this process resulted in more material being lost than the amount of carbon necessary to account for the fluorine addition required by $(CF_3)_2CFCF(CF_3)_2$. The formation of carbon on NaF and KF pellets is a well known phenonemen when in contact with C_3F_6 at elevated

temperatures, and the complete degradation of some of the C_3F_6 might not be unexpected. The reactor was opened; carbon was observed in the CsF powder.

The mechanism proposed in the previous work is quite suitable for the products obtained:



The absence of isohexane is evidence that tetramethylethylene was not formed and then fluorinated to tetramethylethane.

Effect of Alkali Metal Fluorides on $CF_3CF_2CF_3$, $CF_3CF=CFCF_3$ and CF_3CN

Christie[9] was unable to oxidize perfluoropropane at temperatures as high as 620° over CsF. Alkali metal fluorides do not seem to affect saturated fluorocarbons.

Young[30] passed perfluorobutene-2 over CsF at a temperature of 350°. No dimerization or isomerization

was observed. The olefin was in its most stable form and could only resonate to a higher energy state. Thus there was no isomerization and no opportunity to form a reactive intermediate.

Dresdner[10] attempted to react perfluoroacetonitrile with nitrogen trifluoride. Over CsF, a temperature of 520° was required. Examination of the products seemed to reveal that no carbon-carbon bonds remained intact. All products were the result of cleavage and fluorination. If CsF catalyzed this reaction, it was not apparent. The nitrile is an energetic structure, but the nitrogen has no affinity for fluorine so, the carbanion had no opportunity to form.

Effect of Cesium Fluoride on $CF_2ClCFClCF_2CF{=}CF_2$

A sample of $CF_2ClCFClCF_2CF{=}CF_2$ was prepared by pyrolizing the sodium salt of Kel-F acid 683. A reactor tube was packed with CsF and heated to 240°. The dichloroolefin was passed through the tube and collected in a Dry Ice trap on the other side. The reactor tube was so tightly packed that a pressure head developed, and some material was lost during the process. The conversion was 80 per cent; the yield of the new isomer was 81 per

cent of the products. The contact time was less than 10 seconds. The new isomer, $CF_2ClCFClCF{=}CFCF_3$, was then dehalogenated quantitatively to give perfluoropentadiene-1,3.

$CF_2ClCFClCF_2CF{=}CF_2$ was unique in that it contained a terminal double bond, and therefore the possibility of isomerizing. It would not be expected to form a reactive intermediate because the new isomer would be energetically favored. The total result of the isomerization would be the loss of a fluorine ion from the allylic position. The mechanism would be classified as a concerted S_N2'.

$$CF_2 = CFCFCFClCF_2Cl \xrightarrow[S_N2']{F^-} CF_3CF = CFCFClCF_2Cl + F^-$$

This mechanism was observed in the isomerization

$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[S_N2']{F^-} (CF_3)_2C{=}CFCF_2CF_3 + F^-$$

and will be observed in the isomerizations of the C_5F_8 isomers. In each case the isomerization is to the lower energy isomer - this was implied in the infrared absorption spectra of these isomers.

Effect of Alkali Metal Fluorides on $CF_2{=}NCF_3$

The $CF_3N{=}CF_2$ was prepared by pyrolysis of the parent perfluorocarbamyl fluoride, $(CF_3)_2NCOF \longrightarrow CF_3N{=}CF_2 +$

COF_2,[17] and was purified by fractionation. The fraction boiling between -33 and -31° was used.

A reactor tube was packed with CsF and heated to 340°. At a contact time of 200 seconds, the conversion of $CF_2=NCF_3$ to products was 76.6 per cent, and the yield of $(CF_3)_2NCF=NCF_3$ was 100 per cent. The azomethine dimer had previously been prepared by J. A. Young[17] in the fluorination of $CF_2=NCF_3$ with AgF_2.

Several attempts were made to react NF_3 with $CF_2=NCF_3$. At 340° and a contact time of 54.5 seconds, no NF_3 was consumed, the conversion to products was 50 per cent and the yield of dimer was 100 per cent.

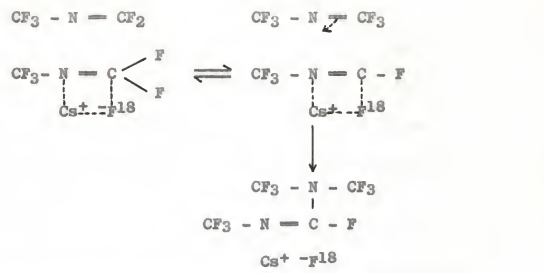
At 450° and a contact time of 30.5 seconds, no NF_3 was consumed, the conversion to products was 65 per cent and the yield of dimer was 100 per cent.

At 537° and a contact time of 31.5 seconds, NF_3 was consumed. The conversion to products was 47 per cent; the yield of dimer was 31.3 per cent and the yield of tetramethylhydrazine was 25 per cent. Tetramethylhydrazine was identified by its boiling point and infrared absorption spectrum.[16,17]

At the time this phase of the work was being completed, Dr. W. H. Christie of ORNL visited this laboratory and

reported on some similar work he had conducted at Oak Ridge[31] - the attempted exchange of F^{18} in CsF^{18} with fluorine in $CF_3N{=}CF_2$. He found that although there was very little exchange, there was 100 per cent conversion of $CF_3N{=}CF_2$ to a dimer at 25 to 80°, and that thereafter the conversion was inversely related to the temperature of dimerization. The monomer was completely absorbed by CsF at the low temperature and could only be desorbed as a dimer at more elevated temperatures. CsF could not be regarded as a catalyst for the reaction between NF_3 and $CF_3N{=}CF_2$. However, CsF appeared to be an excellent ionic catalyst for the dimerization at relatively low temperatures as well as at higher thermal conditions.

The mechanism for the ionic dimerization can not include an exchange of fluorines between CsF and azomethine, and therefore must differ with the mechanism proposed for fluorocarbon olefins. The mechanism proposed is a four center bond between CsF and a molecule of azomethine, reversing the polarity of that azomethine molecule and making reaction with another azomethine molecule possible. The molecule not associated with CsF becomes activated and adds to the molecule associated with CsF, releasing the CsF from its original four centered bond.



There was no possibility of forming tetramethylhydrazine because the system lacked a source of fluorine. $CF_2{=}NCF_3$ was prepared at 600° over NaF so it would not be expected to decompose at temperatures below that. The yield of dimer decreased as the temperature was increased - probably because the adsorption of $CF_3N{=}CF_2$ on CsF decreased.

When NF_3 was used as a reagent, the production of dimers proceeded by a similar mechanism at lower temperatures. In the vicinity of 500°, the NF_3 formed free radicals, and the fluorine atom was responsible for the production of tetramethylhydrazine.

$$CF_3 - N = CF_2 \overset{F\cdot}{\rightleftharpoons} (CF_3)_2N\cdot \longrightarrow (CF_3)_2NN(CF_3)_2$$

Effect of Alkali Metal Fluorides on the Isomerization of $CF_2=CFCF_2CF=CF_2$

Production and identification of isomers studied

Perfluoropentyne-2 was the major product when pentadiene-1,4 was passed over CsF at any temperature from 200 to 520°. Accordingly all the products from these runs were combined and fractionated. A large quantity of perfluoropentyne-2, which had less than a 2° boiling range, was collected from this fractionation. Chromatographic analysis on two different columns and under a variety of flow rates indicated that this material was very pure.

Henne and Latif[18] reported making this compound while attempting to exhaustively fluorinate $CF_2CF_2CF_2CCl=CCl$ with antimony (V) fluoride. They reported weak infrared absorptions at 4.9 and 5.1 microns. This compound had the reported absorptions, but were very, very weak. They also reported a boiling point of +8°. The boiling point of this material was +3.3 to +3.6°. The molecular weight was 212. An NMR spectrum of this material confirmed its structure (see Table II).

Perfluoropentadiene-1,3 was a new compound. In making pentadiene-1,4 an olefin $CF_2ClCFClCF_2CF=CF_2$ was dehalogenated.

A sample of the dichloro-olefin was prepared and then passed over CsF at 240° at a very rapid rate. A dichloro-olefin boiling at 73 to 75° was produced (the 5,6-dichloropentene-1 boiled at 90°). The wavelength of the double bond absorption had increased, so it was assumed that the new olefin was 5,6-dichloropentene-2. The new olefin was dehalogenated with zinc in dry isopropyl alcohol to give an olefin with a boiling point of 26.3 to 26.9°. An elemental analysis confirmed the empirical formula, and an NMR spectrum confirmed the structure (see Table II). The infrared spectrum was different from that of each of the other isomers (see Table I).

Perfluoromethylcyclobutene-1 was a major product when pentadiene was passed over NaF at 440°. It could not be purified by fractionation because of the proximity of the boiling points of the other isomers. Therefore the mixture of isomers containing over 50 per cent methylcyclobutene-1 was separated chromatographically. The product of the separation contained a small amount of impurity, a material that would not separate from methylcyclobutene-1. An infrared absorption spectrum of a sample rich in the impurity indicated a compound very similar to methylcyclobutene-1. Because methyl-

cyclobutene-1 is believed to be produced by isomerization of methylcyclobutene-3, and because of similarities in the infrared absorption spectra, the impurity was believed to be methylcyclobutene-3.

Methylcyclobutene-1 had a molecular weight of 212 and the correct elemental analysis. It boiled at 11.0 to 11.9° and had an infrared absorption spectrum that was not like any other isomer (see Table I). An NMR spectrum confirmed this structure (see Table II). The olefin was oxidized by $KMnO_4$ in acetone. An acid was produced that had the correct NMR spectrum (F^{19}) for $CF_3COCF_2CF_2COOH$ (see Table II). The acid was titrated potentiometrically; it had two end points - one at pH2 and another at pH8. The end point at pH2 probably represented neutralization of the acid, and the one at pH8 probably represented haloform formation from the ketone. The molecular weight, calculated from the acid number, approached the proper value of the hydrated keto acid as the material was dried with P_2O_5, but the minimum error was 2.6 per cent. This was consistent with the infrared absorption spectrum which indicated some hydration of the ketone. Employing standard organic techniques, a crystalline solid believed to be the

phenyl hydrazone was formed. It had a sharp melting point of 150 to 151°.

Perfluorocyclopentene was prepared by fluorinating $CF_2CF_2CF_2CCl{=}CCl$. The fluorination was novel in this work in that a flask equipped with a stirrer and reflux condenser was used. CoF_3 was placed in the bottom of the flask with the dichloro-olefin. The slurry was stirred and heated until there was considerable reflux. After two days the volatile material was removed. Chromatographic analysis indicated that two materials were present - 60 per cent a new material and 40 per cent the dichloro-olefin. Fractionation did not separate the two materials, so all the material was placed in dry isopropyl alcohol with zinc and heated. A water condenser allowed only low-boiling materials to escape. An almost quantitative yield of cyclopentene was collected. The material that escaped through the condenser was passed through P_2O_5, and a product obtained that was better than 99 per cent pure cyclopentene. Henne and Latif[18] had prepared this material and reported the infrared absorption of the unsaturation and the boiling point. The material compared favorably in these two physical properties. The infrared absorption spectrum was exactly the same as the material formed in the isomerization of pentadiene-1,4

over carbonized NaF pellets (see Table I). The infrared absorption spectrum was used in later stages of the work for preliminary identification of this isomer.

Table III

Isomerization of C_5F_8 Isomers over Selected Catalysts

Experiment Number	Isomer Treated	Catalyst System	Reactor Temperature	Contact Time, Seconds	Pentyne-2	Methylcyclobutene-2	Methylcyclobutene-1	Pentadiene-1,3	Cyclopentene	Pentadiene-1,4
1.	Pentyne-2	CsF	240°	150	100					
2.	Pentyne-2	CsF	440°	114	88	3	3	3		3
3.	Pentyne-2	CsF	520°	118	40		30	20		10
4.	Pentyne-2	NaF	440°	137	99.5			0.5		
5.	Pentyne-2	NaF	520°	83	92.0		4	4.0		
6.	Pentyne-2	None**	360°		99					
7.	Pentyne-2	None	440°	137	99					
8.	Pentyne-2	None*	32°		50					
9.	Methylcyclobutyne-1	CsF	240°	200	1		97			2
10.	Methylcyclobutyne-1	NaF	440°	130	9		85		3	3
11.	Methylcyclobutyne-1	None**	360°		3		91	6		
12.	Methylcyclobutyne-1	None*	32°		0.1		99.9			
13.	Pentadiene-1,3	CsF	240°	140	85	1	1	1	1	1
14.	Pentadiene-1,3	NaF	320°	125	60		24.8	15.2		
15.	Pentadiene-1,3	NaF	440°	98	60		40			
16.	Pentadiene-1,3	None*	32°					100		
17.	Pentadiene-1,3	None**	360°		10			60	25	3

Table III - Continued

Experiment Number	Isomer Treated	Catalyst System	Reactor Temperature	Contact Time, Seconds	Pentyne-2	Methylcyclobutene-2	Methylcyclobutene-1	Pentadiene-1,3	Cyclopentene	Pentadiene-1,4
18.	Cyclopentene	CsF	240°	100					100	
19.	Cyclopentene	NaF	340°	140					100	
20.	Cyclopentene	NaF	440°	115					100	
21.	Cyclopentene	NaF	520°	88	1				97	2
22.	Cyclopentene	None**	360°		98		0.5		99.5	
23.	Cyclopentene	None*	32°						100	
24.	Pentadiene-1,4	CsF	240°	150	98					
25.	Pentadiene-1,4	NaF	160°	160						99
26.	Pentadiene-1,4	NaF	220°	115	1	1	1	1		96
27.	Pentadiene-1,4	NaF	440°	213	27		58		10	5
28.	Pentadiene-1,4	NaF	440°	100	35	0.5	55	0.5	4	5
29.	Pentadiene-1,4	C	440°	370	20			40		40
30.	Pentadiene-1,4	None**	360°		2			4		94
31.	Pentadiene-1,4	None*	32°					2		98
32.	Pentadiene-1,4	C+NaF	240°	150						97
33.	Pentadiene-1,4	C+NaF	340°	213		5	20	10	65	
34.	Pentadiene-1,4	C+NaF	440°	124			40	5	50	3

*Subjected to 10^7 roentgens of gamma radiation.
**In a heavywalled glass ampule, maximum pressure 11 atmospheres.

Correlation and evaluation of all reactions involving the C_5F_8 isomers

a. General.

In this section no attempt was made to reproduce the data that appeared in the Experimental chapter. The quantity of data that must be interelated would cause discontinuity in presentation. Therefore, all the data concerning the C_5F_8 isomers has been tabulated in Table III. Each reaction has been assigned a number for reference purposes.

b. Gamma radiation.

It was evident from Experiments 8, 12, 16, 23 and 31 that all isomers except pentyne-2 were essentially unaffected by gamma radiation. Pentyne-2 formed a white fluffy polymer. The polymer was not evaluated, but was stable to over 400°; it contracted at 428° and decomposed at 458°.

c. Heat.

The behavior of each isomer was studied by heating without a catalyst. Pentyne-2 was not affected (Experiment 6), nor was cyclopentene (Experiment 22). This implied that these two isomers, once formed, would not be affected by heat alone. Pentadiene-1,4 underwent a

small amount of isomerization to pentadiene-1,3 and pentyne-2 (Experiment 30). If carbon was used as a catalyst, there was considerable conversion to pentadiene-1,3 and pentyne-2 (Experiment 29). In each case one half as much pentyne-2 was formed as pentadiene-1,3. Pentadiene-1,3 was converted to methylcyclobutene-1, cyclopentene and pentyne-2 (Experiment 17). Methylcyclobutene-1 was converted in small quantities to pentadiene-1,3 and pentyne-2, and there was marked polymerization to a dark-brown solid (Experiment 11).

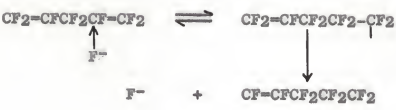
This evidence indicated that when pentadiene-1,4 was converted to pentyne-2, the attack was probably concerted, because pentyne-1,3 does not form pentyne-2 exclusively under these conditions. Methylcyclobutene-1 appeared to undergo extensive polymerization, but the C_5F_8 isomers remaining were starting material and a small amount of pentadiene-1,3.

d. Carbon - sodium fluoride pellets.

The reactor tube employed had been used in cracking perfluoropropylene. Each NaF pellet had been impregnated with a small amount of very fine carbon. The carbon probably interferred with the very close contact required

for catalysis, and products were obtained that were different from products obtained over pure NaF pellets.

At 240°, pentadiene-1,4 did not react appreciably (Experiment 32), but at 340° (Experiment 33) the major product was cyclopentene. This product could only result by a thermal attack on the pentadiene-1,4 - activating the terminal carbon atom.



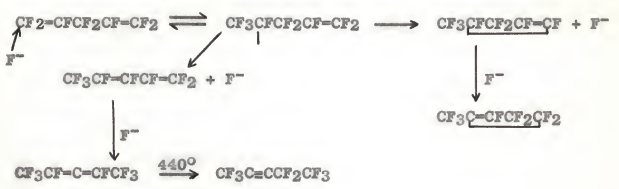
Once cyclopentene was formed, it was inert to attack by a fluoride ion or heat (Experiments 13, 14, 15 and 17).

e. Sodium fluoride.

A temperature of 440° was required to isomerize pentadiene-1,4 in appreciable yields (Experiments 25, 26, 27 and 28). The major products were methylcyclobutene-1 and pentyne-2. A small quantity of cyclopentene was also produced, but that was probably by attack of the number 2 carbon, and will be considered a separate mechanism from the main reaction. It was also observed that pentyne-2 was inert under these conditions (Experiment 4), while pentadiene-1,3, if formed, would be

converted to pentyne-2 (Experiment 15).

The reaction mechanism proposed therefore was:



The reaction over NaF gave several products, but the major product was the result of the electron cloud being located on the second carbon (very similar to propylene). If a stronger catalyst was used, two such centers might form - precluding the internal cyclization to form methylcyclobutene.

f. Cesium fluoride.

In all previous work it has been demonstrated that CsF was the most effective catalyst of the alkali metal fluoride family. The shift of an external double bond had been observed, and there was subsequent displacement of an allylic fluoride ion. When pentadiene was subjected to CsF, an attack at both ends of the molecule was expected, pushing off the allylic fluorides:

$$CF_2{=}CFCF_2CF{=}CF_2 \longrightarrow CF_3CF{=}C{=}CFCF_3 + 2F^-$$

(F^- at the 1- and 4-positions)

The compound that should have been produced was the allene. Very recently, this compound was produced by Miller[32] at less than 100°. The allene would be unstable at 240° and would form pentyne-2:

$$CF_3CF{=}C{=}CFCF_3 \xrightarrow{240^\circ} CF_3C{\equiv}CCF_2CF_3$$

When pentadiene-1,4 was passed over CsF there was 98 per cent conversion to pentyne-2 (Experiment 24). The reaction may have been converted or step wise, because pentadiene-1,3 would be converted to pentyne-2 (Experiment 13). None of the other isomers could have been made because they were all stable under these conditions (Experiments 1, 9, 18), and would have appeared as a product. The conversion of pentadiene-1,4 to pentyne-2 may be represented by the equation:

$$CF_2{=}CFCF_2CF{=}CF_2 \xrightarrow{F^-} CF_2CF{=}CF{=}CF_2 \xrightarrow{F^-} CF_3CF{=}C{=}CFCF_3$$

$$\searrow$$

$$CF_3C{\equiv}CCF_2CF_3$$

The difference in the reactions over NaF and CsF appeared to be related to the activity of the catalyst.

NaF was a weaker catalyst, and allowed a reactive anion to form by not forcing the double bonds to the most central position. Thus resonance and shifts in the electron cloud would be expected. If the least energetic form was obtained, the compound was not activated by the catalyst, but if as in propylene, there was resonance between two isomers, activation could result.

When CsF was used as a catalyst, the double bonds were moved very effectively to central positions with very little resonance between alternate isomers, and no activation was observed.

CONCLUSIONS

A perfluoro-olefin that has a terminal double bond can be expected to be affected by alkali metal fluorides. If a double bond of a lower bond energy can be formed without breaking a carbon-carbon bond, the olefin will be isomerized to that structure. If the two possible isomers are equivalent, the olefin is activated and susceptible to ionic or free radical attack.

Perfluoropropylene is activated by alkali metal fluorides. It may then undergo ionic additions or, if attacked by a free radical, will participate in free radical reactions.

Longer-chain olefins tend to isomerize a double bond to the most internal position. By using a more or a less active catalyst, the distribution of isomers obtained will vary. The order of the catalytic activity of the alkali metal fluorides is in decreasing activity: CsF, RbF, KF, NaF.

Azomethine dimerized when in contact with CsF. It could be fluorinated with NF_3, but the reaction was similar

to fluorination with AgF_2, in that fluorine atoms were involved.

Either a flow system or a sealed vessel may be used for the isomerizations. The dimerization of azomethine and propylene gave better yields in sealed tubes with CsF, probably because of increased pressure and the longer contact time. The reaction of free radicals with propylene gave better yields of the addition product in a flow system, mostly because the number of products produced was smaller.

Generally, CsF will activate propylene sufficiently at about 300° in a flow system for free radical additions or for dimerization. In a sealed reaction vessel, 200° is sufficient for dimerization. CsF will isomerize olefins at 240° in a flow system. If NaF is used as a catalyst, isomerization will occur at 340° in a flow system. At 440°, the isomerization is more extensive and some dimer is formed.

CsF did not catalyze additions to azomethine; it adsorbed azomethine and catalyzed an ionic dimerization. The mechanism would be very complicated because it involved association with the crystal lattice to increase the polarity of one molecule of azomethine, loss of a fluorine

ion to another molecule of azomethine, and a bond forming between the nitrogen of the second molecule of azomethine and the carbon that lost the fluorine in the first molecule. This mechanism is consistent with the product obtained and the observation that CsF does not exchange with azomethine.

CsF can not isomerize propylene because both isomers are equivalent. The resonance between the two isomers is increased, resulting in an increase in electron density in the vicinity of the center carbon. Propylene is then considered activated, and may undergo ionic reactions. If the activated propylene molecule is attacked by a free radical, it will undergo free radical reactions.

Olefins containing a double bond of higher energy will be isomerized to a double bond position of lower energy. As bond energy is inversely proportional to wavelength, infrared absorption can be used to predict the feasibility or direction of isomerization. The isomerization is believed to progress by a concerted S_N2' mechanism.

BIBLIOGRAPHY

1. J. H. Simons, Editor, "Fluorine Chemistry," Academic Press Inc., New York, 1950, I, p. 423.

2. C. Slesser and S. R. Schrom, Editors, "National Nuclear Energy Series," McGraw-Hill Book Co., Inc., New York, 1951, VII-I, p. 717.

3. Simons, Op. Cit., I, p. 432.

4. T. A. Gens, Doctoral Dissertation, University of Florida (1957).

5. J. H. Fried and W. T. Miller, Jr., J. Am. Chem. Soc., 81, 2078 (1959).

6. W. T. Miller, Jr., J. H. Fried and H. Goldwhite, J. Am. Chem. Soc., 82, 399 (1960).

7. A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corporation, New York, 1958, p. 32.

8. G. K. Falk, "Catalytic Action," The Chemical Catalog Company, Inc., New York, 1922, p. 142 - 149.

9. W. Christie, Doctoral Dissertation, University of Florida (1958).

10. R. D. Dresdner, F. N. Tlumac and J. A. Young, J. Am. Chem. Soc., 82, 5831 (1960).

11. L. C. Yen, Master of Science Thesis, University of Florida (1957).

12. T. M. Reed, III, J. F. Walter, R. R. Cecil and R. D. Dresdner, Ind. and Eng. Chem., 51, 271 (1959).

13. J. H. Simons and Co-workers, Electrochemical Society Journal, 95, 47 (1947).

14. C. Colburn, F. Johnson, A. Kennedy, K. McCollum, L. Metzger and C. Parker, J. Am. Chem. Soc., 81, 6397 (1957).

15. C. B. Colburn, Private Communication.

16. M. Hauptschein, M. Braid and F. E. Lawlor, J. Org. Chem., 23, 323 (1958).

17. J. A. Young, W. S. Durrell and R. D. Dresdner, J. Am. Chem. Soc., 81, 1587 (1959).

18. A. L. Henne and K. A. Latif, J. Am. Chem. Soc., 76, 610 (1954).

19. W. T. Miller, U. S. Patent 2,668,182 (1954).

20. C. B. Colburn and A. Kennedy, J. Am. Chem. Soc., 80, 5004 (1958).

21. S. Morrow, D. Perry and M. Cohen, J. Am. Chem. Soc., 81, 6338 (1959).

22. J. W. Frazer, J. Inorg. Nucl. Chem., 11, 1166 (1959).

23. R. D. Dresdner, F. N. Tlumac and J. A. Young, J. Inorg. Nucl. Chem., 14, 299 (1960).

24. J. Gould, Private Communication.

25. W. T. Miller and A. T. Dittman, J. Am. Chem. Soc., 78, 2793 (1956).

26. A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,381 (1946).

27. G. C. Rogers and G. H. Cady, J. Am. Chem. Soc., 73, 3523 (1951).

28. J. H. Simons, W. H. Pearlson and W. K. Jines, U. S. Patent 2,494,064 (1950).

29. R. N. Haszeldine and J. E. Osborne, J. Chem. Soc., 1955, 3880.

30. J. A. Young, Private Communication.

31. W. H. Christie, F. N. Tlumac, R. D. Dresdner and J. A. Young, Abstract of Papers, 138th Meeting, Am. Chem. Soc., New York, Sept. 1960, p. 18M.

32. W. T. Miller, Private Communication.

BIOGRAPHICAL SKETCH

Fred Norman Tlumac was born in Little Ferry, New Jersey, on February 2, 1931.

He attended Rutgers University from September, 1948, until June, 1952, receiving the degree of Bachelor of Science in Dairy Manufacturing.

In September, 1952, he entered the U. S. Army and served as an Infantry Officer until June, 1954.

In June, 1954, he became Assistant to the Chief Chemist at Burry Biscuit Company, Elizabeth, New Jersey. At the same time, he attended Graduate School at Seton Hall University, South Orange, New Jersey, in the evening division.

He entered the University of Florida in September, 1956, as a graduate student in Chemistry and received a degree of Master of Science in August, 1958. He currently holds a graduate assistantship.

Mr. Tlumac is married to the former Barbara Anne McKenna and is the father of two children.

He is a member of Gamma Sigma Epsilon and Sigma Xi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 5, 1961

Dean, College of Arts and Sciences

Dean, Graduate School

SUPERVISORY COMMITTEE:

Chairman

Co-Chairman